

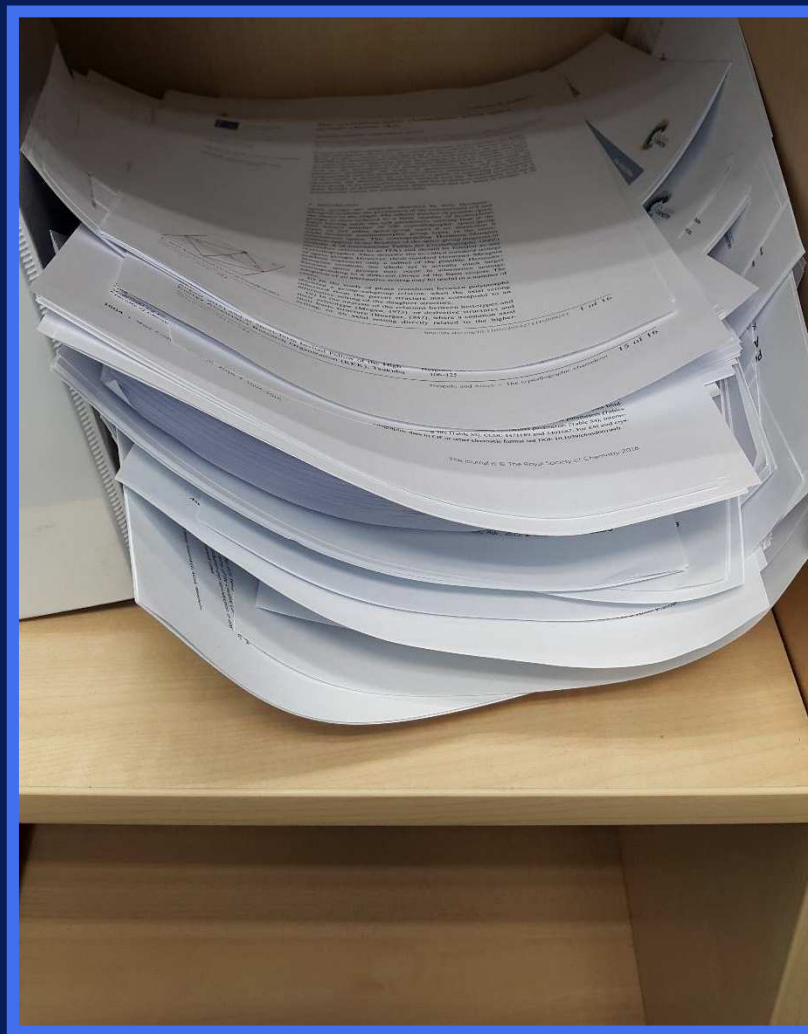


Recent Advances in the Understanding of Element(Lone-Pair)... π (Arene) Interactions Operating as Supramolecular Synthons

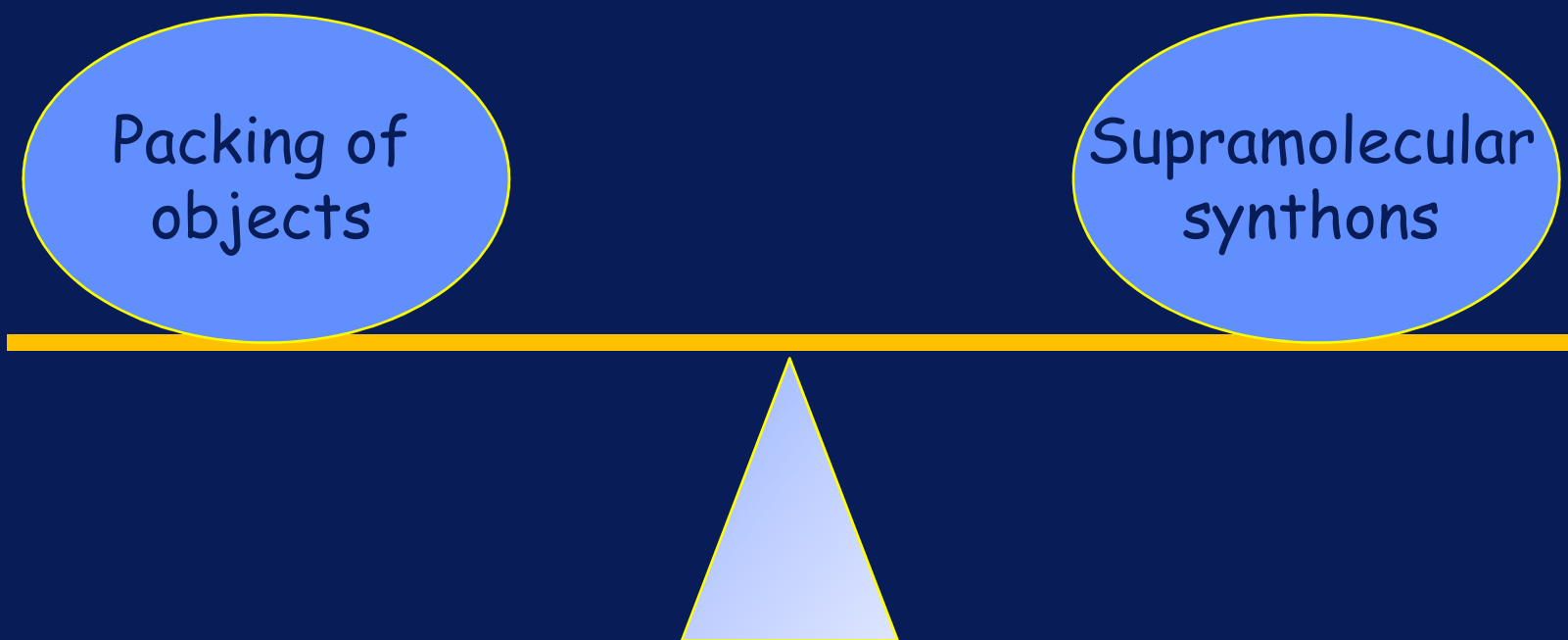
Edward R.T. Tiekink
Research Centre for Crystalline Materials
Faculty of Science and Technology

1st SEACCE, September 2016

Factors that Make SEACCE Great!



Factors that Control Molecular Packing



Points of Contact/Recognition Between Molecules in Crystals

Hydrogen-bonding & coordinate bonds

$\pi \cdots \pi$, $C-H \cdots X$, $C-H \cdots \pi$, halogen bonding
 $M \cdots X$, $M \cdots M$

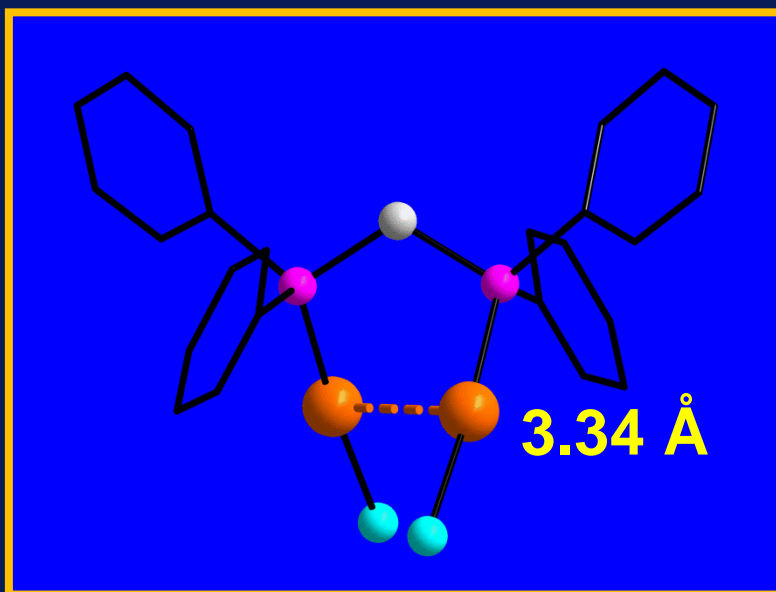
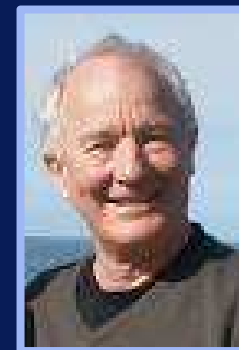
Others:

$C-H \cdots \pi$ (chelate), lone-pair $\cdots \pi$, tetrel,
pnictogen, chalcogen...

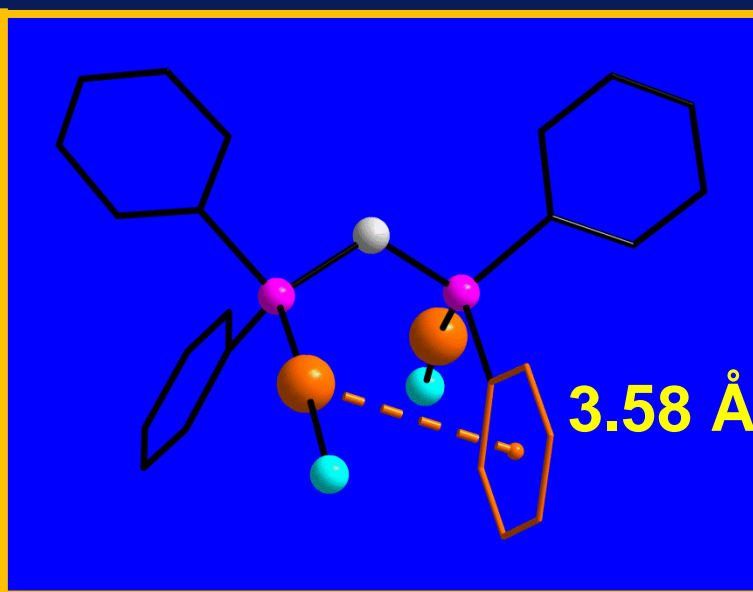




Polymorphs of $(\text{dppm})(\text{AuCl})_2$



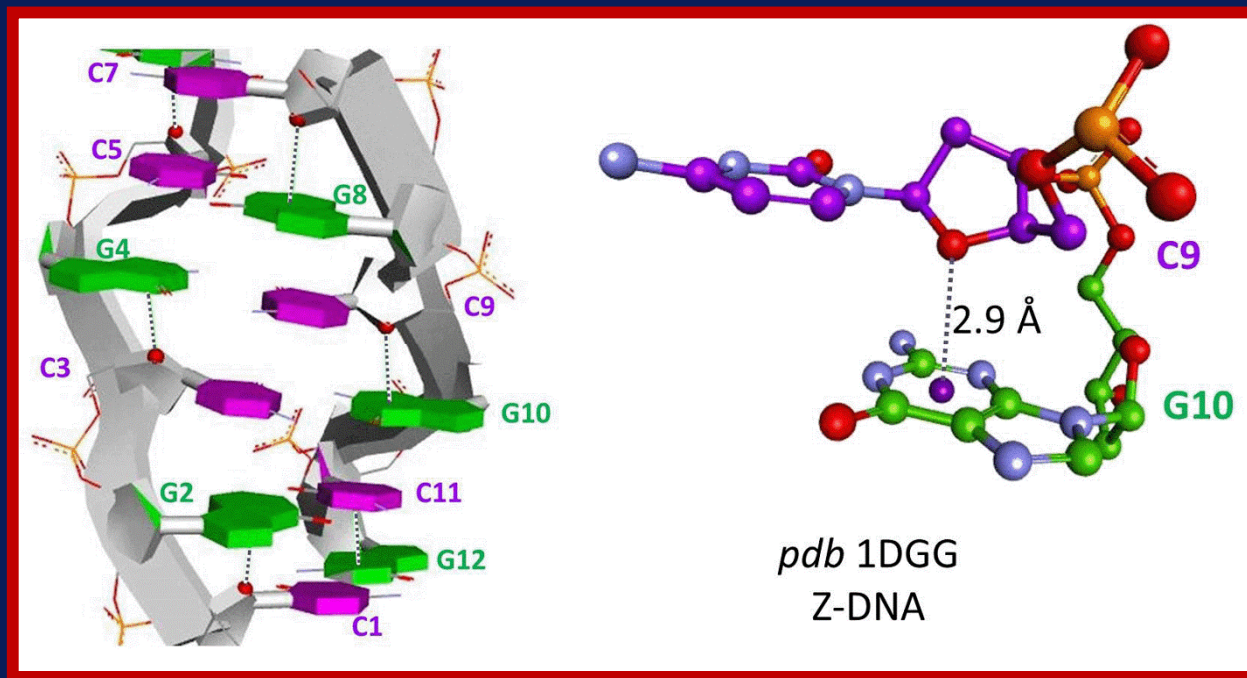
Schmidbaur *et al.* (1977)



Healy (2003)

Bio-inspiration

(O)lone pair... π (guanidinium) interaction stabilises the left-handed Z-DNA duplex



400 proteins: 1.5 kJ mol⁻¹ to 5.1 kJ mol⁻¹

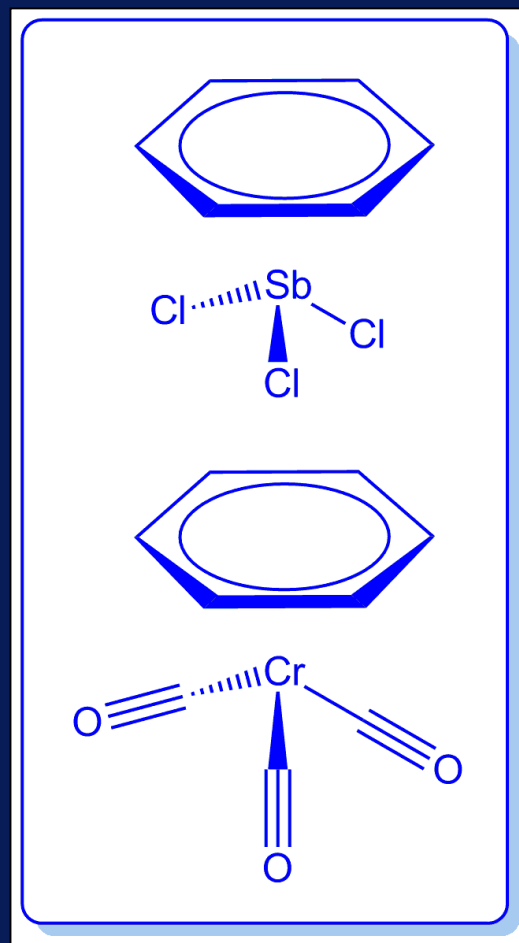
Egli & Gessner, *PNAS*, 1995, **92**,180; Jain *et al.*, *Protein Sci.*, 2009, **18**, 595

The pre-bio-inspiration

Menšutkin complexes



1874 - 1938

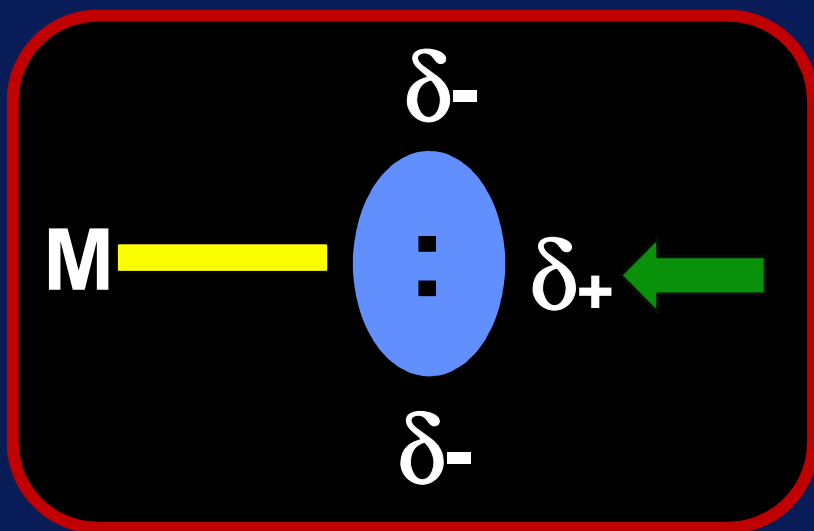


Davies, *J. Chem. Educ.*, 1938, **15**, 203; Schmidbaur & Schier, *Organometallics*, 2008, **27**, 2361.

Bonding Considerations

$M \dots \pi(\text{arene})$ - HOMO donating to metal

$M(\text{Ip}) \dots \pi(\text{arene})$ - cf. halogen bonding



i.e. polar positive hole

As to Bi: 6-9 kJ.mol^{-1}

Expt'l (Sb): 20-40 kJ.mol^{-1}

Energy considerations:

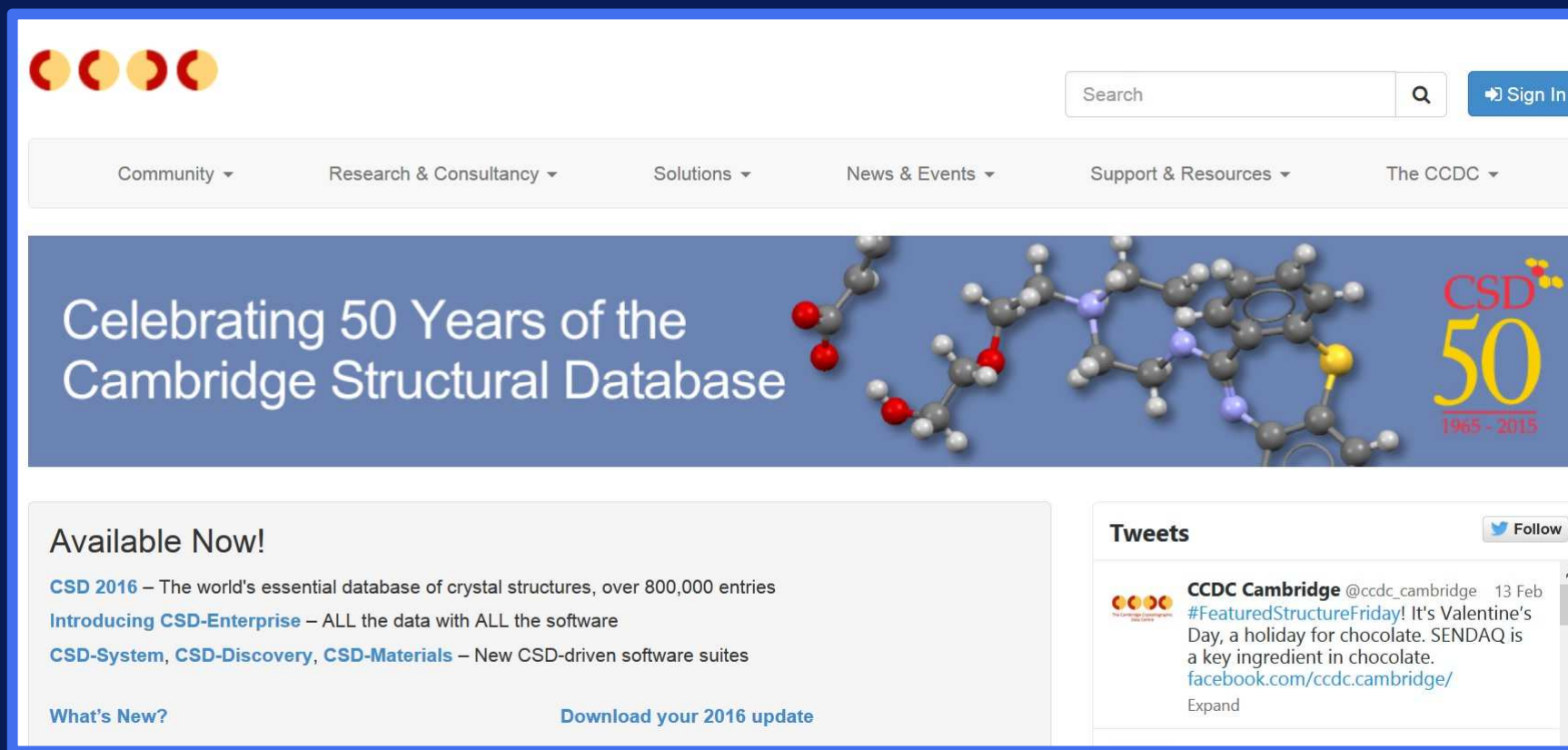
	kJ mol^{-1}
$\text{O}-\text{H}\cdots\text{O}$	20 - 65

$\pi\cdots\pi$	8 - 40
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$\text{C}-\text{H}\cdots\text{O}$	4 - 16
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$\text{C}-\text{H}\cdots\pi$	1 - 8
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Data mining: > 800,000 deposited structures



The screenshot shows the CCDC website homepage. At the top, there is a navigation bar with the CCDC logo (four colored circles) on the left, a search bar with the text "Search" and a magnifying glass icon, and a "Sign In" button on the right. Below the navigation bar is a horizontal menu with the following items: "Community", "Research & Consultancy", "Solutions", "News & Events", "Support & Resources", and "The CCDC". The main banner features the text "Celebrating 50 Years of the Cambridge Structural Database" on the left, a molecular structure visualization in the center, and a large "CSD 50" logo with "1965 - 2015" on the right. Below the banner, there is a section titled "Available Now!" with the following text: "CSD 2016 – The world's essential database of crystal structures, over 800,000 entries", "Introducing CSD-Enterprise – ALL the data with ALL the software", and "CSD-System, CSD-Discovery, CSD-Materials – New CSD-driven software suites". At the bottom of this section are links for "What's New?" and "Download your 2016 update". On the right side, there is a "Tweets" section with a "Follow" button. The first tweet is from "CCDC Cambridge @ccdc_cambridge" dated "13 Feb" and contains the text: "#FeaturedStructureFriday! It's Valentine's Day, a holiday for chocolate. SENDAQ is a key ingredient in chocolate. facebook.com/ccdc.cambridge/". Below the tweet is an "Expand" link.

Community Research & Consultancy Solutions News & Events Support & Resources The CCDC

Celebrating 50 Years of the Cambridge Structural Database

CSD 50 1965 - 2015

Available Now!

CSD 2016 – The world's essential database of crystal structures, over 800,000 entries

Introducing CSD-Enterprise – ALL the data with ALL the software

CSD-System, CSD-Discovery, CSD-Materials – New CSD-driven software suites

What's New? Download your 2016 update

Tweets

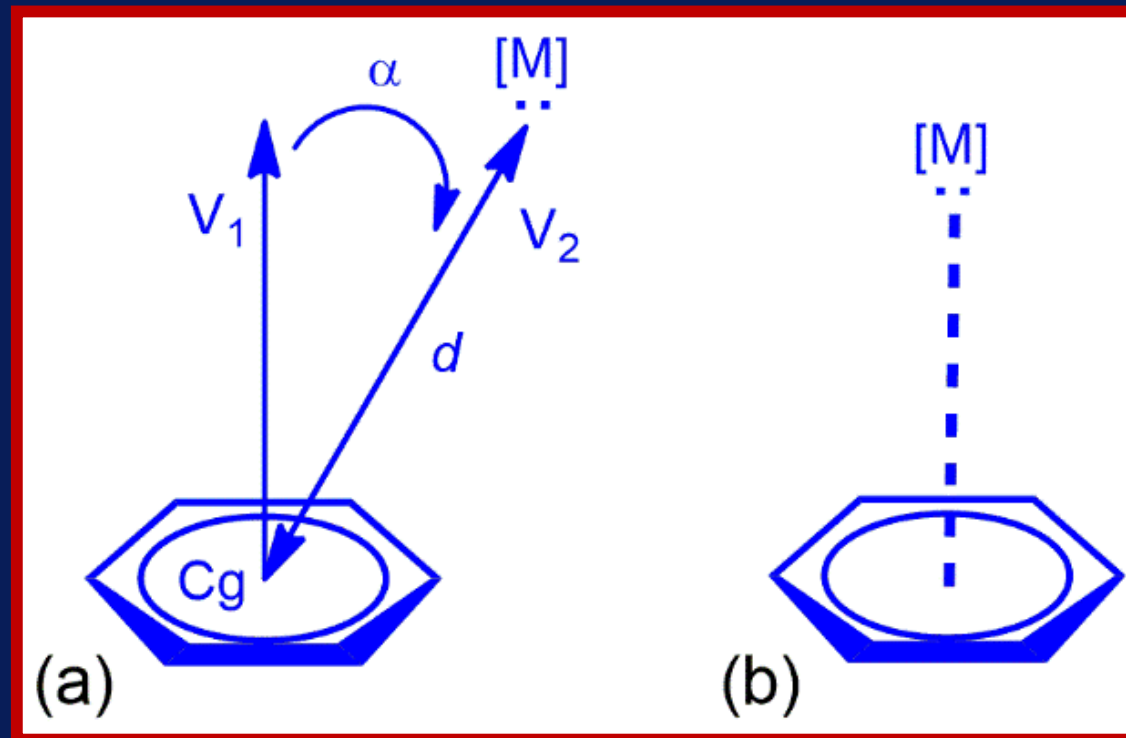
CCDC Cambridge @ccdc_cambridge 13 Feb

#FeaturedStructureFriday! It's Valentine's Day, a holiday for chocolate. SENDAQ is a key ingredient in chocolate. facebook.com/ccdc.cambridge/

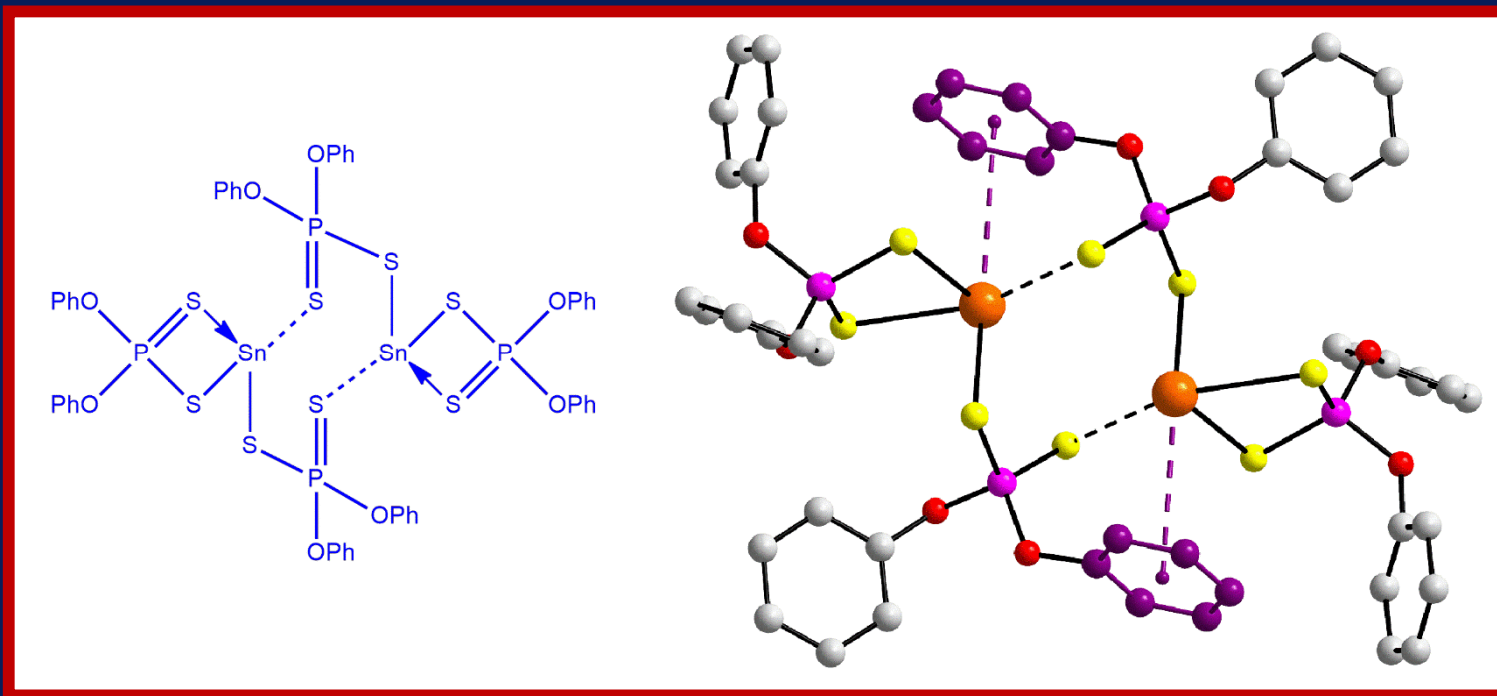
Expand

<http://www.ccdc.cam.ac.uk/>

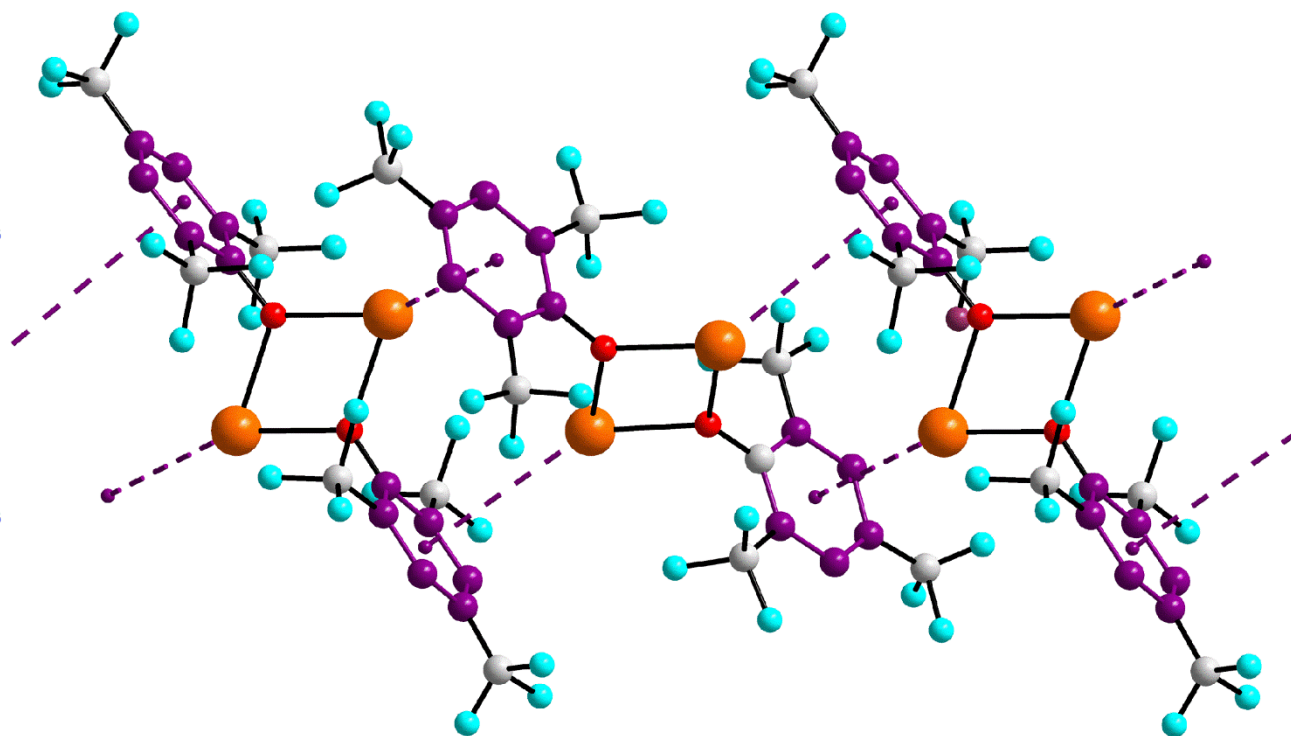
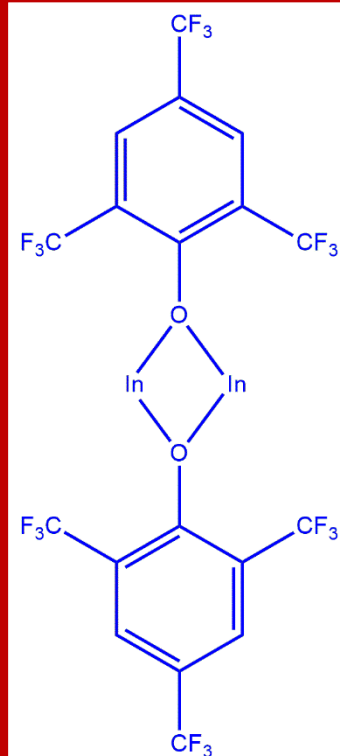
Search Protocols



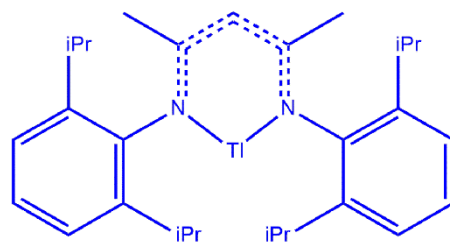
Search Protocols



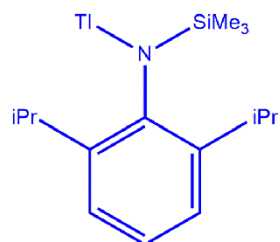
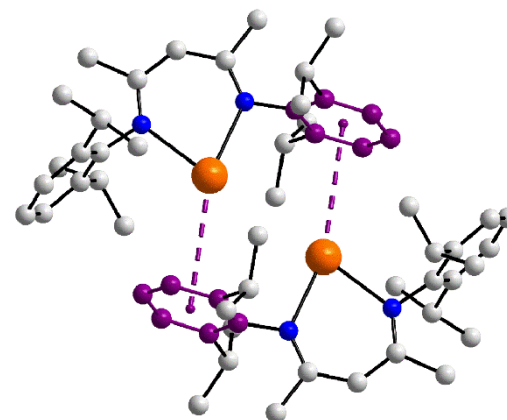
Cooperation: **EXCLUDED**



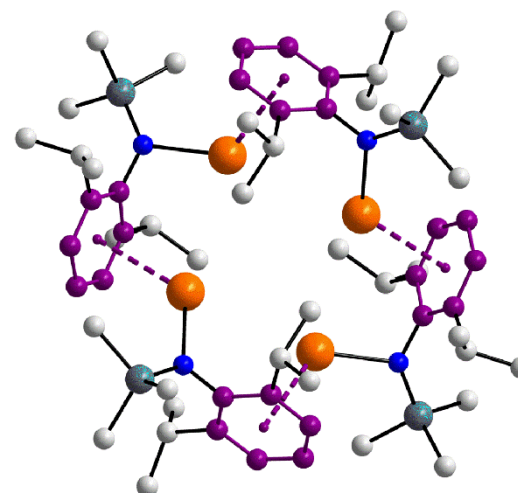
Binuclear, indium(I): 1-D



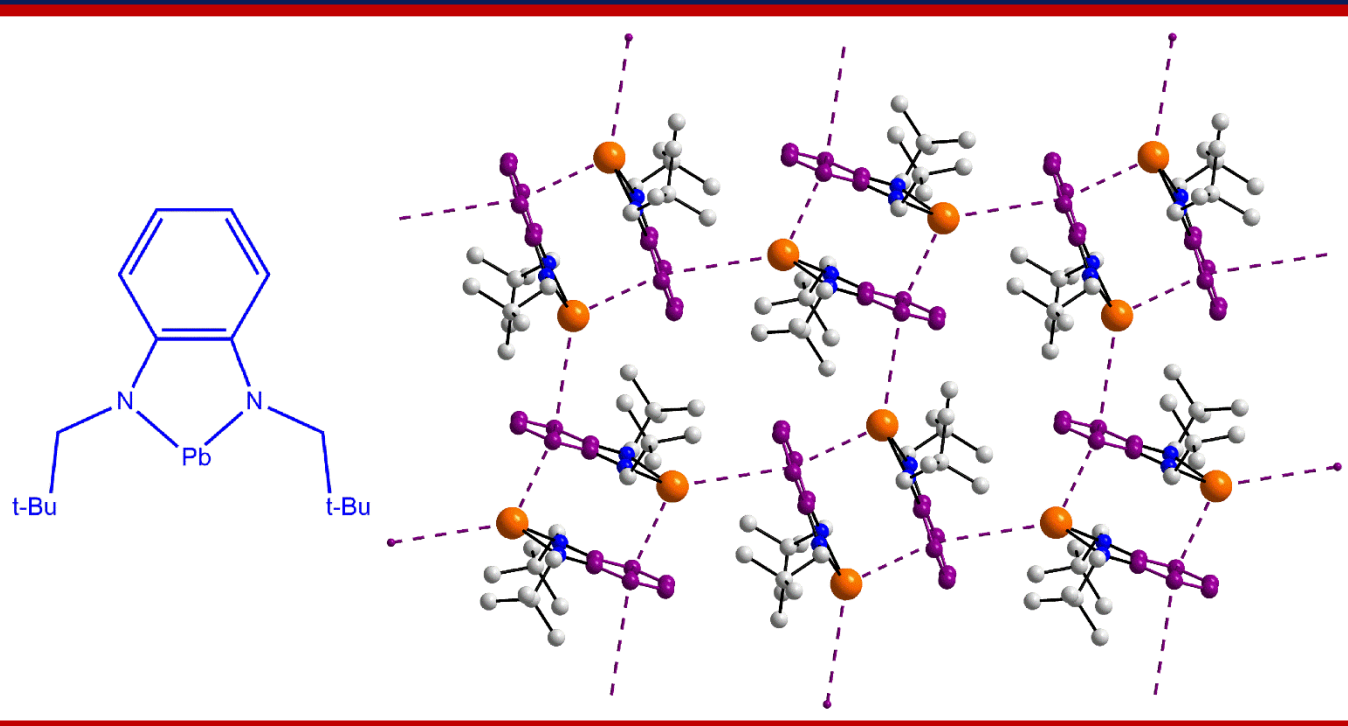
(a)



(b)

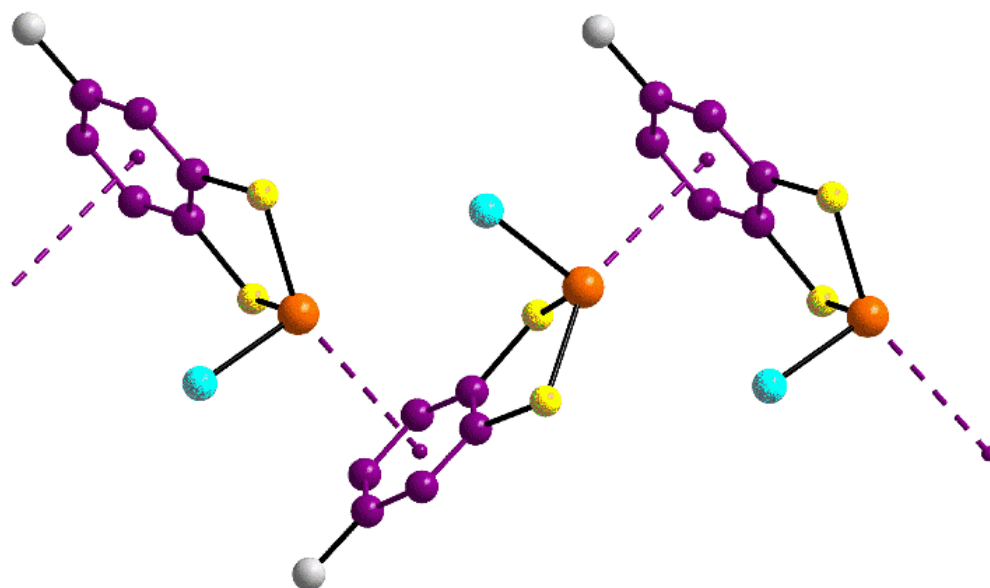
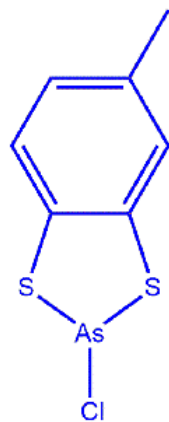


Mononuclear, thallium(I): O-D

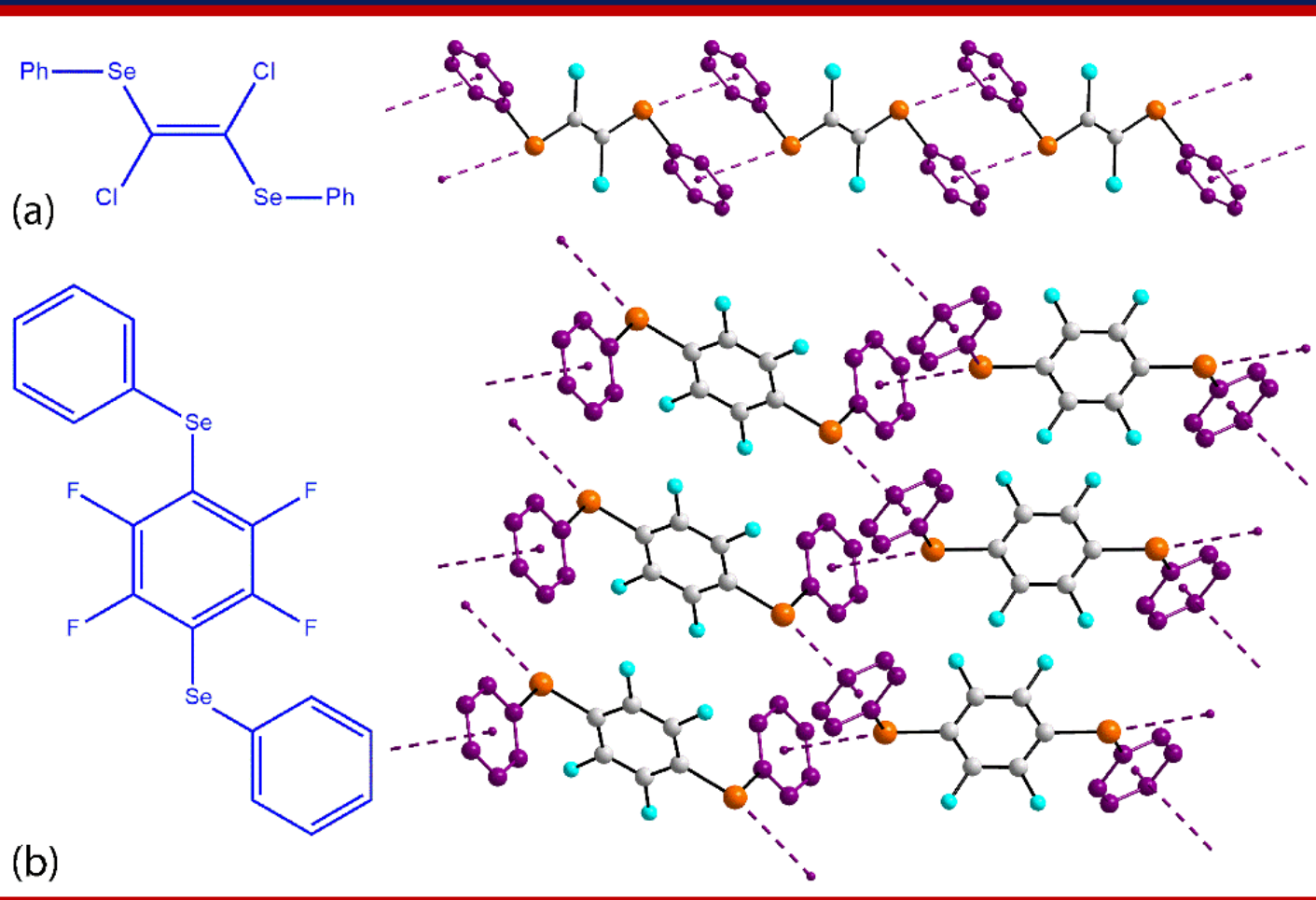


Mononuclear, lead(II): 2-D

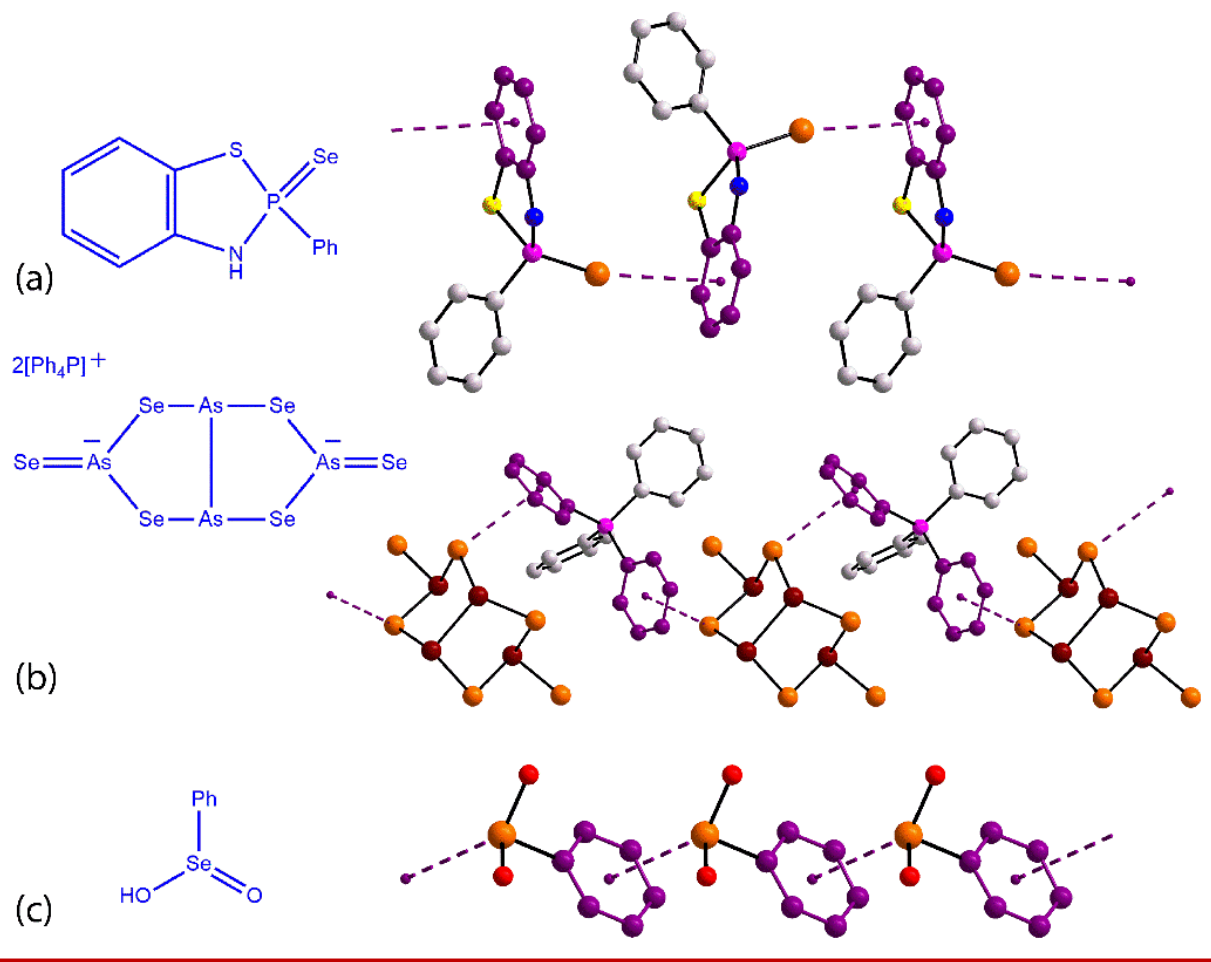
(b)



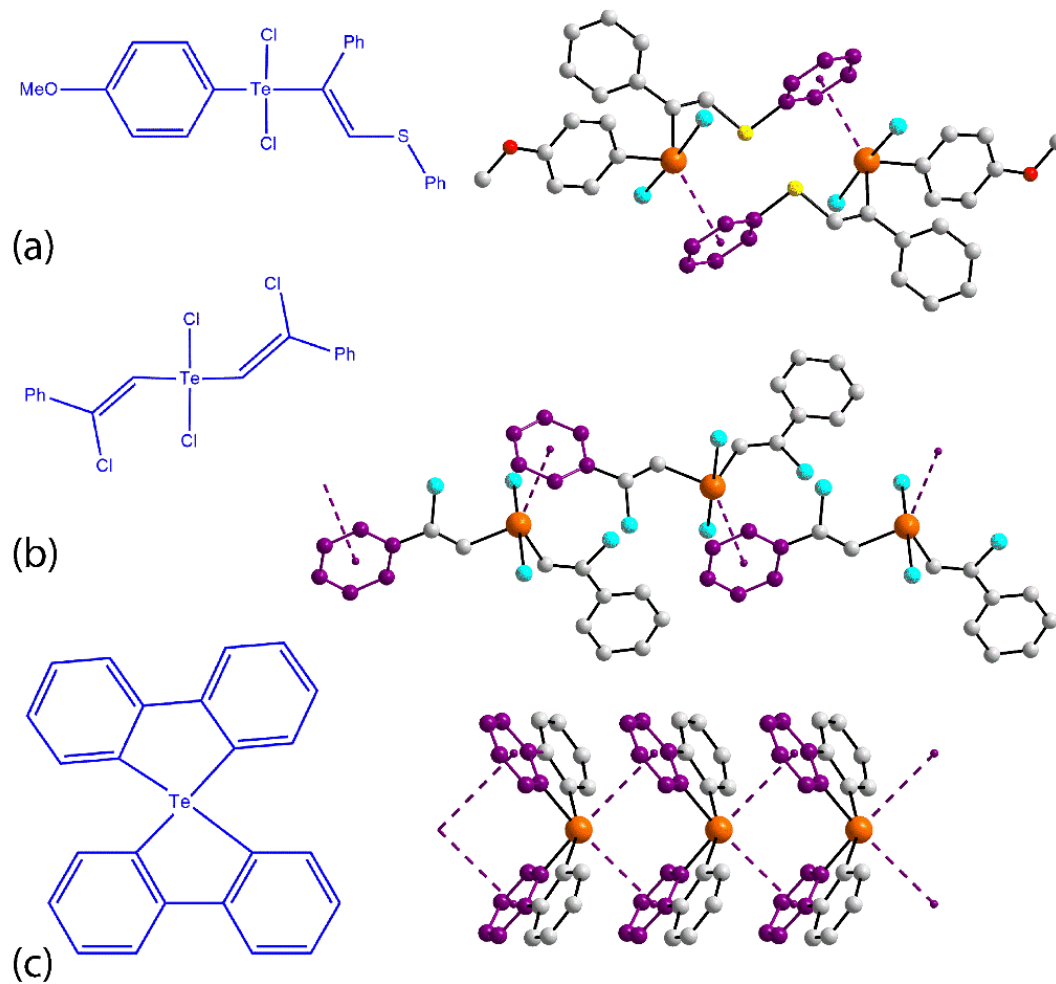
Mononuclear, arsenic(III): 1-D



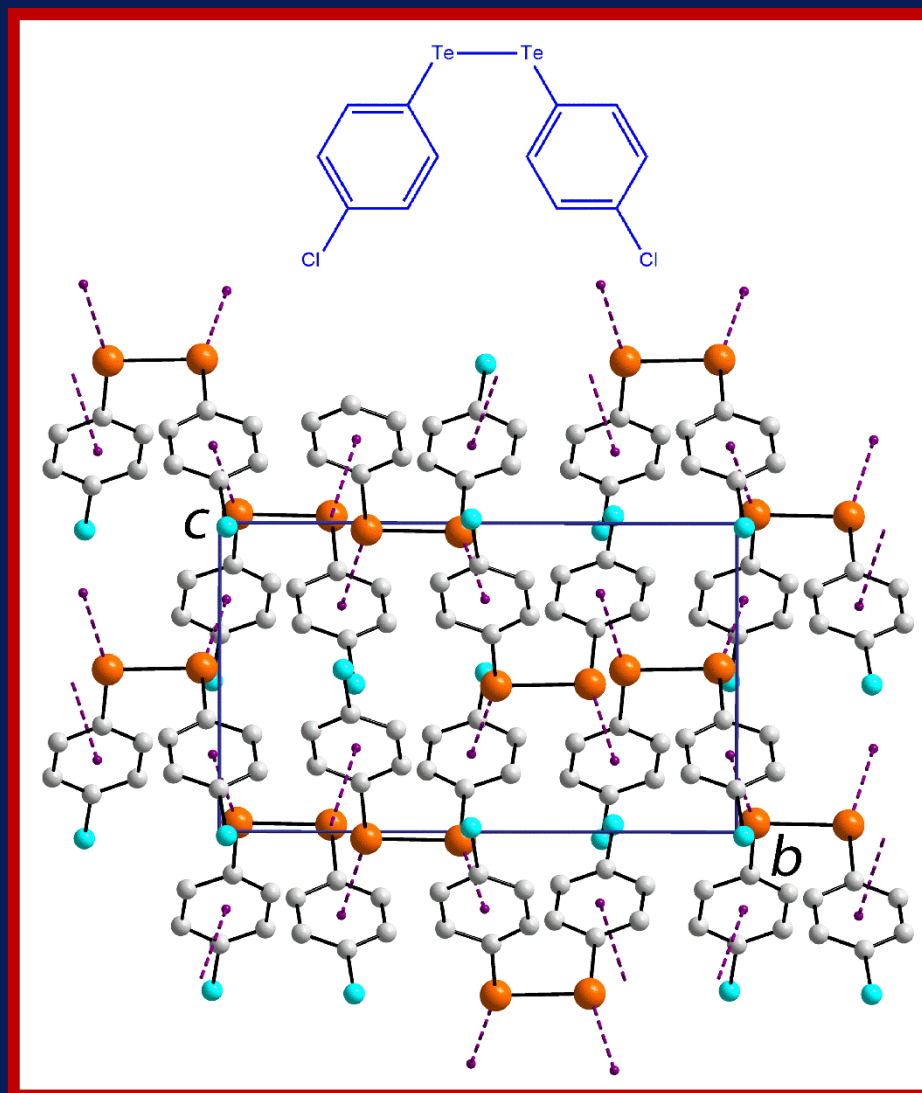
Binuclear, selenium(IV): 1-D & 2-D



Selenium(II, IV): 1-D



Tellurium(IV): 0-D & 1-D

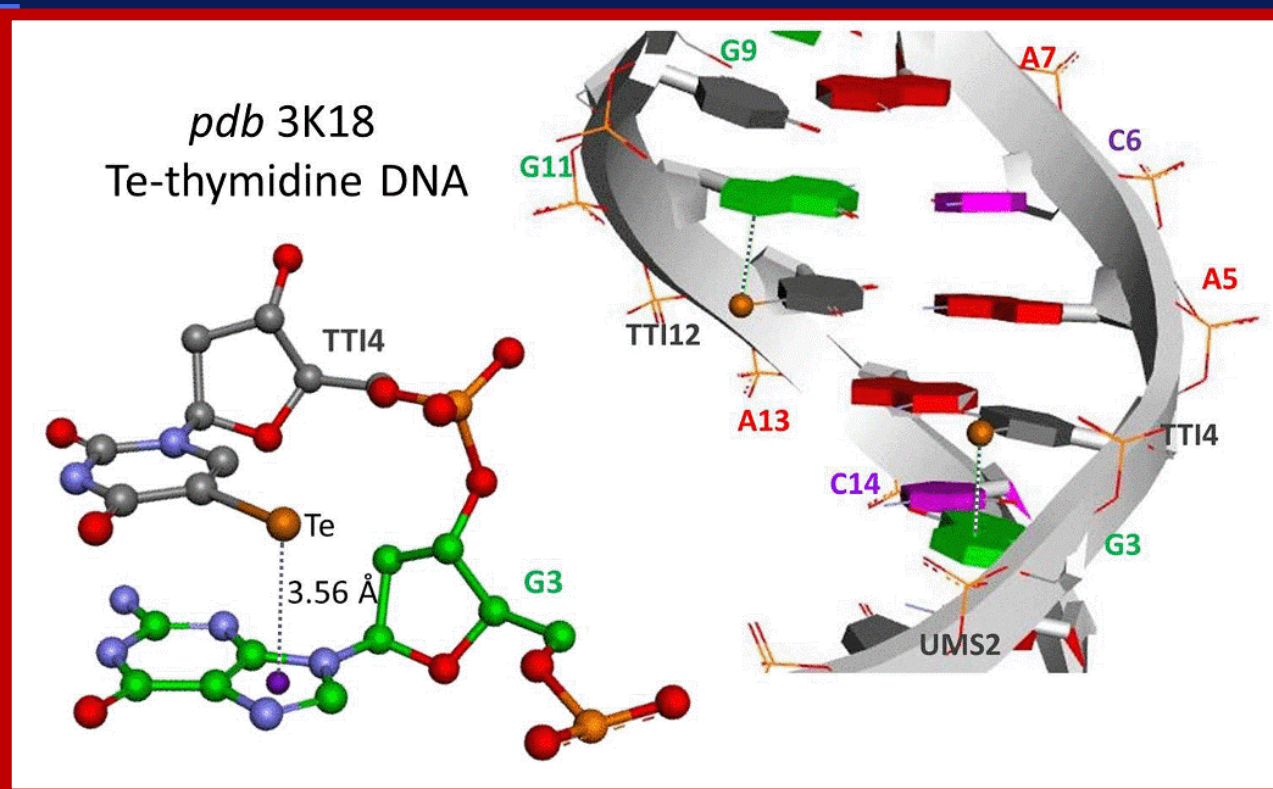


Tellerium(II): 3-D

Biological Example



Ignez
Caracelli



Overview

Maximum adoption: 14% TI

Often:

occur in co-operation with other synthons
intramolecular

No distance/angle correlations

Included in the PLATON output

Complete description of molecular packing should
include $M(\text{lone-pair})\dots\pi(\text{arene})$ interactions



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